



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C11D 3/22, 17/06</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 95/34625</b> <b>(43) International Publication Date:</b> 21 December 1995 (21.12.95)
<b>(21) International Application Number:</b> PCT/US95/06291 <b>(22) International Filing Date:</b> 18 May 1995 (18.05.95)  <b>(30) Priority Data:</b> 08/258,808                      13 June 1994 (13.06.94)                      US  <b>(71) Applicant:</b> THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).  <b>(72) Inventors:</b> STEARNS, Charles, Louis; 1562 Jonquilmeadow Drive, Cincinnati, OH 45240 (US). STRAUSS, Daniel, Louis; 6530 Bluebird Court, Mason, OH 45040 (US).  <b>(74) Agents:</b> REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		<b>(81) Designated States:</b> CA, CN, JP, MX, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR; IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> DETERGENT COMPOSITION CONTAINING ANIONIC SURFACTANTS AND WATER-SOLUBLE SACCHARIDES  <b>(57) Abstract</b>  A detergent composition in form of agglomerates is provided. The detergent composition contains from about 1 % to about 50 % by weight of a deterative surfactant system. The surfactant system itself includes, by weight of the surfactant system, at least about 30 % of a sulfated surfactant selected from alkyl sulfates, alkylethoxy sulfates, secondary alkyl sulfates and mixtures thereof. The detergent includes from about 0.1 % to about 5 % of a water-soluble saccharide selected from the group consisting of cellubiose, glucose, maltose, lactose, ribose, and lactulose mixtures thereof. Also, the detergent composition includes at least about 1 % by weight of a detergency builder to enhance cleaning. The surfactant system, saccharide and builder are agglomerated to form detergent agglomerates having a density of at least about 650 g/l. The anionic surfactants in the detergent composition have significantly improved dissolution in aqueous laundering solutions, especially those kept at cold temperatures, i.e. 5 °C to 30 °C.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

## DETERGENT COMPOSITION CONTAINING ANIONIC SURFACTANTS AND WATER-SOLUBLE SACCHARIDES

5

FIELD OF THE INVENTION

The present invention is generally directed to an agglomerated compact detergent composition having improved solubility in cold temperature laundering solutions. More particularly, the invention is directed to a detergent composition containing high levels of a sulfated surfactant selected from the group consisting of alkyl sulfates (also referenced herein as "AS"), alkyl ethoxy sulfates (also referenced herein as "AES"), and secondary alkyl sulfates (also referenced herein as "SAS") and mixtures thereof, and selected amounts of water-soluble saccharides, together which improve the overall solubility or dispersability of the composition in cold temperature washing solutions (e.g. 5°C to 30°C) and high water hardness conditions (e.g. 7 grains/gallon). For purposes of producing a high density, compact detergent composition, the detergent of the invention is in the form of detergent agglomerates rather than spray dried granules.

15

BACKGROUND OF THE INVENTION

Typically, conventional detergent compositions contain mixtures of various surfactants in order to remove a wide variety of soils and stains from surfaces. For example, various anionic surfactants, especially the alkyl benzene sulfonates, are useful for removing particulate soils, and various nonionic surfactants, such as the alkyl ethoxylates and alkylphenol ethoxylates, are useful for removing greasy soils.

20

While the art is replete with a wide variety of surfactants for those skilled in the art of detergent formulation, most of the available surfactants are specialty chemicals which are not suitable for routine use in low cost items such as home laundering compositions. The fact remains that many home-use laundry detergents still comprise one or more of the conventional alkyl benzene sulfonates or primary alkyl sulfate surfactants. Another class of surfactants which has found use in various compositions where emulsification is desired comprises the secondary alkyl sulfates. The conventional secondary alkyl sulfate surfactants are available as generally pasty, random mixtures of sulfated linear and/or partially branched alkanes.

25

The limited solubility of alkyl sulfate surfactants including both primary and secondary alkyl sulfates is especially prevalent in modern granular laundry detergents which are typically used in cold temperature (e.g. 5°C to 30°C) washing solutions and are formulated in "condensed" or "compact" form for low dosage usage. For the consumer, the smaller package size attendant with compact detergent products provides for easy storage and handling. For the manufacturer, unit storage costs, shipping costs and packaging costs are lowered.

30

35

The manufacture of acceptable compact or condensed granular detergents has its difficulties. In a typical compact detergent formulation, the so-called "inert" ingredients such as

sodium sulfate are substantially eliminated. However, such ingredients do play a role in enhancing solubility of conventional detergents. As a consequence, compact detergents often suffer from solubility problems, especially in cold temperature laundering solutions. Moreover, conventional compact or low density detergent granules are usually prepared by spray drying processes which  
5 result in extremely porous detergent particles that are quite amenable to being dissolved in aqueous washing solutions. By contrast, compact detergents are typically comprised of less porous, high density detergent particles which are less soluble, e.g. agglomerates. Thus, since the compact form of granular detergents typically comprise particles or granules which contain high levels of detergent ingredients with little or no room for solubilizing agents, and since such particles are intentionally  
10 manufactured at high bulk densities, the net result can be a substantial problem with regard to in-use solubility.

In the art of detergency, sugars have been to some extent used to replace sodium silicate for purposes of improving solubility of spray dried granular detergents. For example, one attempt in the past was directed to a spray-dried detergent composition containing sugars and a seed crystal for  
15 calcium carbonate to provide improved solubility. However, only "spray-dried" detergent compositions having low concentrations of sulfated surfactants have been considered in the past. Thus, the problems associated with modern day compact detergents having densities which are much higher (650 g/l or more) have not been addressed, as yet. Generally speaking, only the highly densified agglomerated detergent compositions encounter a much more difficult problem of  
20 dissolving in cold temperature laundering solutions as compared to less dense spray-dried detergents.

Accordingly, despite the disclosures in the art, there remains a need for an agglomerated, high density detergent composition which has improved water solubility, especially in cold temperature washing solutions. This need is especially prevalent in the art of compact or high  
25 density detergents currently being used by consumers.

#### BACKGROUND ART

The following patents disclose the use of sugars in detergents compositions:  
Davies et al, U.S. Pat. No. 4,908,159 (Lever Brothers Co.); Davies et al, U.S. Pat. No. 4,755,318 (Lever Brothers Co.); McCallion et al, U.S. Pat. No. 4,655,782 (Lever Brothers Co.); Cheng, U.S.  
30 Pat. No. 4,414,130 (Colgate-Palmolive Co.); Finck, U.S. Pat. No. 3,821,118 (Colgate-Palmolive Co.); JP Pat. No. 52094304 (Yuken Kogyo KK); JP 58125797 (Shiseido KK); JP 60060196 (Kanebo KK); JP 61238894 (Sunstar KK); JP 04146998 (Lion Corp.).

The following patent discloses secondary alkyl sulfates: Rossall et al, U.S. Patent No. 4,235,752.

### SUMMARY OF THE INVENTION

The present invention meets the needs identified above by providing a detergent composition in the form of agglomerates which exhibits improved solubility or dissolution of the anionic surfactants in cold temperature washing solutions as well as under high water hardness conditions. The detergent composition comprises a surfactant system having a high level of a sulfated surfactant selected from the group of alkyl sulfates, alkyl ethoxy sulfates, secondary alkyl sulfates and mixtures thereof, in combination with a water-soluble saccharide. Other adjunct detergent ingredients may also be included in the detergent agglomerates which form the detergent composition. Additionally, the composition surprisingly exhibits improved water solubility despite being in the form of high density agglomerates and being subjected to cold temperature washing solutions.

As used herein, the phrase "improved solubility" means that the solubility of the anionic surfactants of the detergent composition is enhanced by at least 5% in the laundering solution when employed in the manner of this invention, as compared to the solubility of the same anionic surfactants per se, under the same test conditions (i.e. water temperature and pH, stirring speed and time, particle size, water hardness, and the like). As used herein, the term "agglomerates" refers to particles formed by agglomerating particles which typically have a smaller mean particle size than the formed agglomerates. All percentages, ratios and proportions used herein are by weight, unless otherwise specified. All documents including patents and publications cited herein are incorporated herein by reference.

In accordance with one aspect of the invention, a detergent composition in the form of agglomerates is provided herein. The detergent composition comprises from about 1% to 50% by weight of a deterative surfactant system. The surfactant system itself comprises, by weight of the surfactant system, at least about 30% of a sulfated surfactant selected from the group consisting of alkyl sulfates, alkyl ethoxy sulfates, secondary alkyl sulfates and mixtures thereof. The detergent composition includes from about 0.1% to about 5% of a water-soluble saccharide selected from the group consisting of cellobiose, glucose, maltose, lactose, ribose, and lactulose mixtures thereof. Also, the detergent composition includes at least about 1% by weight of a detergency builder to enhance cleaning. The surfactant system, water-soluble saccharide, and builder are agglomerated to form detergent agglomerates having a density of at least about 650 g/l. The detergent composition has improved solubility in aqueous laundering solutions. Thus, the solubility of the sulfated surfactant (AS, AES and/or SAS) is enhanced by at least 5%, preferably 10 to 50%, over those same surfactants alone under the same test conditions in aqueous washing solutions at cold temperatures, i.e. 5°C to 30°C.

In another embodiment of the invention, the sulfated surfactant is a mixture of alkyl sulfate and alkyl ethoxy sulfate surfactants. Further, the detergent composition may include adjunct ingredients selected from the group consisting of bleaches, bleach activators, suds suppressers and soil release agents.

In a preferred embodiment, the detergency builder is selected from the group consisting of carbonates, zeolites and mixtures thereof. The surfactant system may further comprise, by weight of the surfactant system, from about 1% to about 50% of a C<sub>10</sub>-C<sub>18</sub> N-alkyl polyhydroxy fatty acid amide for use as an adjunct surfactant. In another embodiment, the composition may include from  
5 about 0.1% to about 15% of a linear alkylbenzene sulfonate surfactant.

In a preferred embodiment of the invention, the detergent composition comprises: (a) at least about 30% by weight of a sulfated surfactant selected from the group consisting of alkyl sulfates, alkyl ethoxy sulfates, secondary alkyl sulfates and mixtures thereof; (b) from about 0.1% to about 5% by weight of sucrose; and (c) at least about 1% by weight of a detergency builder; wherein  
10 the surfactant system, saccharide and builder are agglomerated to form detergent agglomerates having a density of at least 650 g/l. The sulfated surfactant of the surfactant system has improved solubility in an aqueous laundering solution and the composition is substantially free of phosphates.

In accordance with another aspect of the invention, a method for laundering soiled fabrics is provided. The method comprises the step of contacting soiled fabrics with an effective amount of a  
15 detergent composition as described herein in an aqueous laundering solution. An effective amount is typically on the order of 1000 to 1500 ppm. Yet another embodiment of the invention is directed to a laundry bar formed from compositions described herein.

Accordingly, it is an object of the present invention to provide a granular detergent composition which has improved solubility, especially in cold temperature washing solutions. It is  
20 also an object of the invention to provide such a detergent composition which has improved biodegradability. These and other objects, features and attendant advantages of the present invention will become apparent to those skilled in the art from a reading of the following detailed description of the preferred embodiment and the appended claims.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

25 The invention is directed to a granular detergent composition having improved solubility in cold temperature laundering solutions. A multitude of consumers around the world launder soiled clothes in conventional washing machines unique to their particular geographic location. Typically, these conventional washing machines launder the soiled clothes in water supplied at relatively cold temperatures, for example in range of 5°C to 30°C, and at high hardness concentrations, e.g. 7  
30 grains/gallon (rich with Ca and Mg ions). Most of the modern day consumers also use compact or condensed laundry detergents to accomplish their laundering needs. Under the aforementioned conditions, solubility of current detergents in aqueous laundering solutions has been a problem, as mentioned previously. This problem is especially exacerbated when the detergent composition has high levels of alkyl sulfates, alkyl ethoxy sulfate and/or secondary alkyl sulfates which are not  
35 particularly amenable to dissolution in cold aqueous laundering solutions. Such surfactants are particularly useful in modern laundry detergents since they minimize or eliminate the need for linear alkylbenzene sulfate surfactants which generally have poor biodegradability. Moreover,

recent compact detergents have strived to limit or eliminate the use of phosphates which are known to increase water solubility. In view of this trend, the water solubility problem is exacerbated further.

It has been found that highly dense, agglomerated detergent compositions can experience improved water-solubility if selected amounts of a water-soluble saccharide are included. Such detergent compositions preferably also include a surfactant system which comprises at least 30%, preferably from about 35% to about 90%, of a sulfated surfactant selected from the group consisting of alkyl sulfates, alkyl ethoxy sulfates, secondary alkyl sulfates and mixtures thereof. Preferably, the detergent composition is in the form of agglomerates and has an overall density of 650 g/l or higher. These features provide the "compact" nature of the detergent composition in accordance with the invention. Preferably, the detergent composition of the invention also comprises at least about 1%, preferably from about 10% to about 40%, and most preferably from about 15% to about 35%, of a detergency builder. The detergent composition may also include one or more of adjunct detergent ingredients. Nonlimiting examples of the detergency surfactant, water-soluble saccharide, detergency builder and adjunct ingredients are described in detail hereinafter.

For purposes of enhancing biodegradability, the detergent agglomerates which form the detergent composition of the invention preferably do not contain phosphates. Further, it is important for the detergent composition to be in the form of "agglomerates" as opposed to spray dried granules. In addition to being amenable for modern compact detergents, this is particularly important since most sulfated surfactants cannot be readily subjected to spray drying processes without causing or creating extremely adverse plumes from the spray drying towers.

The "improved solubility" achieved by the detergent composition is concerned with enhanced solubility of the anionic surfactants contained in the surfactant system, i.e. AS, AES, SAS or LAS if used. Preferably, the improvement represents at least a 5% increase in solubility of these anionics in the wash solution over the solubility of the same surfactants if they were dissolved alone or without being contained in a detergent composition as defined herein. More preferably, the solubility improvement is from about 10% to about 50%. As those skilled in the art will appreciate, any comparison of anionic surfactant solubility should be completed under the same laundering conditions, e.g. water temperature, hardness and pH, stirring speed and time, and particle size. Typical anionic surfactant solubility improvements are set forth in the Examples hereinafter.

Those skilled in the art should also appreciate the numerous ways in which the amount of the surfactant system in the washing solution can be determined. For example, in the so-called "catSO<sub>3</sub>" titration technique, samples of the aqueous laundering solution containing the detergent composition can be taken after one minute and filtered with 0.45 mm nylon filter HPLC, after which the filtered solution can be titrated with a cationic titrant, which can be commercially purchased, e.g. from Sigma Chemical Company under the trade name Hyamine, in the presence of anionic

dyes. From the foregoing, the amount of anionic surfactant which was dissolved in the washing solution can be determined.

#### Water-Soluble Saccharide

It has been found that the solubility of high-content alkyl sulfate, alkyl ethoxy sulfate and/or secondary alkyl sulfate ("sulfated" surfactant system) compact detergent composition in the form of agglomerates can be increased by incorporating a water-soluble saccharide selected from the group consisting of glucose, maltose, cellobiose, lactose, ribose, and lactulose mixtures thereof into the composition. Other mono-, di-, and poly- saccharides and derivatives thereof may be used in the compositions herein without departing from the scope of the invention. The saccharide repeating unit can have as few as five carbon atoms or as many as fifty carbon atoms consistent with water solubility. To that end, the preferred detergent composition of the invention comprises from about 0.1% to about 5%, more preferably from about 0.5% to about 4%, and most preferably from about 2% to about 4% by weight of the water-soluble saccharide. The most preferred water-soluble saccharide is sucrose for its availability, inexpensiveness and performance. By "water-soluble" in the present context, it is meant that the saccharide is capable of forming a clear solution or a stable colloidal dispersion in distilled water at room temperature at a concentration of 0.01 g/l.

#### Surfactant System

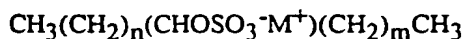
The surfactant system in the detergent composition must include a sulfated surfactant selected from the group consisting of alkyl sulfates, alkyl ethoxy sulfates, secondary alkyl sulfates, and mixtures thereof. As mentioned previously, the anionic surfactants in the surfactant system of the invention, i.e. AS, AES, and/or SAS, have improved solubility and more particularly, on the order of 5% or higher. Optionally, the surfactant system may contain one or more of additional surfactants, nonlimiting examples of which are provided hereinafter.

The surfactant system preferably includes conventional primary alkyl sulfate surfactants have the general formula



wherein R is typically a linear C<sub>10</sub>-C<sub>20</sub> hydrocarbyl group and M is a water-solubilizing cation. Branched-chain primary alkyl sulfate surfactants (i.e., branched-chain "PAS") having 10-20 carbon atoms can also be used herein; see, for example, European Patent Application 439,316, Smith et al, filed 21.01.91, the disclosure of which is incorporated herein by reference (Included in the term "alkyl" is the alkyl portion of acyl groups). Included in the surfactant system are the C<sub>10</sub>-C<sub>18</sub> alkyl alkoxy sulfates ("AE<sub>x</sub>S"; especially EO 1-7 ethoxy sulfates).

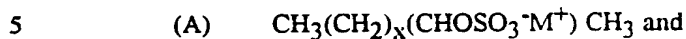
Conventional secondary alkyl sulfate surfactants can also be used herein and include those materials which have the sulfate moiety distributed randomly along the hydrocarbyl "backbone" of the molecule. Such materials may be depicted by the structure





wherein m and n are integers of 2 or greater and the sum of m + n is typically about 9 to 17, and M<sub>n</sub> is a water-solubilizing cation.

More preferably, a selected secondary (2,3) alkyl sulfate surfactant is used herein which comprises structures of formulas A and B



for the 2-sulfate and 3-sulfate, respectively. Mixtures of the 2- and 3-sulfate can be used herein. In formulas A and B, x and (y+1) are, respectively, integers of at least about 6, and can range from about 7 to about 20, preferably about 10 to about 16. M is a cation, such as an alkali metal, ammonium, alkanolammonium, alkaline earth metal, or the like. Sodium is typical for use as M to prepare the water-soluble (2,3) alkyl sulfates, but ethanolanmonium, diethanolammonium, triethanolammonium, potassium, ammonium, and the like, can also be used. It is preferred that the secondary (2,3) alkyl sulfates be substantially free (i.e., contain less than about 20%, more preferably less than about 10%, most preferably less than about 5%) of such random secondary alkyl sulfates.

The preparation of the secondary (2,3) alkyl sulfates of the type useful herein can be carried out by the addition of  $\text{H}_2\text{SO}_4$  to olefins. A typical synthesis using  $\alpha$ -olefins and sulfuric acid is disclosed in U.S. Patent 3,234,258, Morris, or in U.S. Patent 5,075,041, Lutz, granted December 24, 1991, both of which are incorporated herein by reference. The synthesis, conducted in solvents which afford the secondary (2,3) alkyl sulfates on cooling, yields products which, when purified to remove the unreacted materials, randomly sulfated materials, unsulfated by-products such as  $\text{C}_{10}$  and higher alcohols, secondary olefin sulfonates, and the like, are typically 90+% pure mixtures of 2- and 3-sulfated materials (up to 10% sodium sulfate is typically present) and are white, non-tacky, apparently crystalline, solids. Some 2,3-disulfates may also be present, but generally comprise no more than 5% of the mixture of secondary (2,3) alkyl mono-sulfates. Such materials are available as under the name "DAN", e.g., "DAN 200" from Shell Oil Company.

If increased solubility of the "crystalline" secondary (2,3) alkyl sulfate surfactants is desired, the formulator may wish to employ mixtures of such surfactants having a mixture of alkyl chain lengths. Thus, a mixture of  $\text{C}_{12}$ - $\text{C}_{18}$  alkyl chains will provide an increase in solubility over a secondary (2,3) alkyl sulfate wherein the alkyl chain is, say, entirely  $\text{C}_{16}$ . The solubility of the secondary (2,3) alkyl sulfates can also be enhanced by the addition thereto of other surfactants such as the material which decreases the crystallinity of the secondary (2,3) alkyl sulfates. Such crystallinity-interrupting materials are typically effective at levels of 20%, or less, of the secondary (2,3) alkyl sulfate.

35

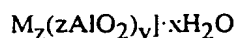
#### Builder

The detergent composition of the invention also includes a detergency builder material to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders

are typically used in fabric laundering compositions to assist in the removal of particulate soils. Inorganic detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates.

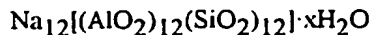
- 5           Examples of silicate builders are the alkali metal silicates, particularly those having a  $\text{SiO}_2:\text{Na}_2\text{O}$  ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum.
- 10       NaSKS-6 has the delta- $\text{Na}_2\text{SiO}_5$  morphology form of layered silicate. It can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula  $\text{NaMSi}_x\text{O}_{2x+1} \cdot y\text{H}_2\text{O}$  wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various
- 15       other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta- $\text{Na}_2\text{SiO}_5$  (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crisping agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

- 20           Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973. Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include
- 25       those having the empirical formula:



wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

- Useful aluminosilicate ion exchange materials are commercially available. These
- 30       aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred
- 35       embodiment, the crystalline aluminosilicate ion exchange material has the formula:



wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites ( $x = 0 - 10$ ) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used, however, in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. Useful succinic acid builders include the  $C_5$ - $C_{20}$  alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986. Other suitable polycarboxylates

are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Fatty acids, e.g., C<sub>12</sub>-C<sub>18</sub> monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

#### Adjunct Surfactants

One or more adjunct surfactants may be included generally at a level of from about 1% to about 50% by weight of the surfactant system described herein. Nonlimiting examples of surfactants useful in conjunction with the surfactants described herein are the C<sub>10</sub>-C<sub>18</sub> alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the C<sub>10</sub>-C<sub>18</sub> glycerol ethers, the C<sub>10</sub>-C<sub>18</sub> alkyl polyglycosides and their corresponding sulfated polyglycosides, and C<sub>12</sub>-C<sub>18</sub> alpha-sulfonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the C<sub>12</sub>-C<sub>18</sub> alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C<sub>6</sub>-C<sub>12</sub> alkyl phenol alkoxyates (especially ethoxylates and mixed ethoxy/propoxy), C<sub>12</sub>-C<sub>18</sub> betaines and sulfobetaines ("sultaines"), can also be included in the overall compositions. The C<sub>10</sub>-C<sub>18</sub> N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C<sub>12</sub>-C<sub>18</sub> N-methylglucamides. See WO 9,206,154. The N-propyl through N-hexyl C<sub>12</sub>-C<sub>18</sub> glucamides can be used for low sudsing. C<sub>10</sub>-C<sub>20</sub> conventional soaps may also be used. If high sudsing is desired, the branched-chain C<sub>10</sub>-C<sub>16</sub> soaps may be used.

Also included in the surfactant system is the conventional C<sub>11</sub>-C<sub>18</sub> alkyl benzene sulfonates (also referenced herein as "LAS"). While the biodegradability of the so-called "LAS" surfactants have been the subject of some concern, the surfactant system herein may include an optimum level, from about 0.1% to about 15% and more preferably from about 3% to about 8% by weight, for improving the overall solubility of the detergent composition without substantially decreasing the overall biodegradability of the present detergent composition. Alternatively, the level of LAS may be included as from about 1% to about 40%, more preferably from about 10% to about 25%, by weight of the surfactant system in the detergent composition.

The surfactant system may also include an amine oxide surfactant. Nonlimiting examples include C<sub>10</sub>-C<sub>18</sub> amine oxides, secondary amine oxides such as dimethyl amine oxide, and tertiary amine oxides having the general formula RR'R"NO in which R is a primary alkyl group containing 8 to 24 carbon atoms; R' is methyl, ethyl, or 2-hydroxyethyl; and R" is independently selected from methyl, ethyl, 2-hydroxyethyl and primary alkyl groups containing 8 to 24 carbon atoms. Additionally, the tertiary amine oxide surfactant may be in hydrated form and have the general formula RR'R"NO nH<sub>2</sub>O wherein R, R' and R" are the same as above and n is 1 or 2. Examples of other tertiary amines suitable for use herein include those containing one or two short-chain groups independently selected from methyl, ethyl, and 2-hydroxyethyl groups, with the remaining valences

of the amino nitrogen being satisfied with long-chain groups independently selected from primary alkyl groups containing 8-24 carbons, e.g., octyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, eicosyl, docosyl, and tetracosyl groups. The primary alkyl groups may be branched-chain groups, but the preferred amines are those in which at least most of the primary alkyl groups have a straight chain.

Exemplary of these tert-amines are N-octyldimethylamine, N,N-didecylmethylamine, N-decyl-N-dodecylethylamine, N-dodecyldimethylamine, N-tetradecyldimethylamine, N-tetradecyl-N-ethylmethylamine, N-tetradecyl-N-ethyl-2-hydroxyethylamine, N,N-di-tetradecyl-2-hydroxyethylamine, N-hexadecyldimethylamine, N-hexadecyldi-2-hydroxyethylamine N-octadecyldimethylamine, N,N-dieicosylethylamine, N-docosyl-N-2-hydroxyethylmethylamine, N-tetracosyldimethylamine, etc.

Additional amine oxide surfactants and methods of making the same, all of which are suitable for use herein, are disclosed by Borland et al, U.S. Patent No. 5,071,594 and Tosaka et al, U.S. Patent No. 5,096,621, incorporated herein by reference.

Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful surfactants are listed in standard texts.

#### Detergent Adjunct Ingredients

The detergent composition can also include any number of additional ingredients. These include detergency bleaches, bleach activators, suds boosters or suds suppressers, anti-tarnish and anticorrosion agents, soil suspending agents, soil release agents, germicides, pH adjusting agents, non-builder alkalinity sources, chelating agents, smectite clays, enzymes, enzyme-stabilizing agents and perfumes. See U.S. Patent 3,936,537, issued February 3, 1976 to Baskerville, Jr. et al., incorporated herein by reference. Also, fabric conditioning agents may be included as an adjunct material such as those described in U.S. Patent 4,861,502, issued August 29, 1989 to Caswell, incorporated herein by reference.

Bleaching agents and activators are described in U.S. Patent 4,412,934, Chung et al., issued November 1, 1983, and in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, both of which are incorporated herein by reference. Chelating agents are also described in U.S. Patent 4,663,071, Bush et al., from Column 17, line 54 through Column 18, line 68, incorporated herein by reference. Suds modifiers are also optional ingredients and are described in U.S. Patents 3,933,672, issued January 20, 1976 to Bartoletta et al., and 4,136,045, issued January 23, 1979 to Gault et al., both incorporated herein by reference.

Suitable smectite clays for use herein are described in U.S. Patent 4,762,645, Tucker et al, issued August 9, 1988, Column 6, line 3 through Column 7, line 24, incorporated herein by reference. Suitable additional detergency builders for use herein are enumerated in the Baskerville patent, Column 13, line 54 through Column 16, line 16, and in U.S. Patent 4,663,071, Bush et al, issued May 5, 1987, both incorporated herein by reference.

Enzymes can be included in the formulations herein for a wide variety of fabric laundering purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, and for the prevention of refugee dye transfer, and for fabric restoration. The enzymes to be incorporated include proteases, amylases, lipases, cellulases, and peroxidases, as well as mixtures thereof. Other types of enzymes may also be included. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their choice is governed by several factors such as pH-activity and/or stability optima, thermostability, stability versus active detergents, builders and so on. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Suitable examples of proteases are the *subtilisins* which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. Another suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S under the registered trade name ESPERASE. The preparation of this enzyme and analogous enzymes is described in British Patent Specification No. 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the trade names ALCALASE and SAVINASE by Novo Industries A/S (Denmark) and MAXATASE by International Bio-Synthetics, Inc. (The Netherlands). Other proteases include Protease A (see European Patent Application 130,756, published January 9, 1985) and Protease B (see European Patent Application Serial No. 87303761.8, filed April 28, 1987, and European Patent Application 130,756, Bott et al, published January 9, 1985).

Amylases include, for example,  $\alpha$ -amylases described in British Patent Specification No. 1,296,839 (Novo), RAPIDASE, International Bio-Synthetics, Inc. and TERMAMYL, Novo Industries.

The cellulase usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, issued March 6, 1984, which discloses fungal cellulase produced from *Humicola insolens* and *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk (*Dolabella Auricula* Solander). suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open to public inspection on February 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P." Other commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673, commercially available from Toyo Jozo Co., Tagata,

Japan; and further *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynt Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. The LIPOLASE enzyme derived from *Humicola lanuginosa* and commercially available from Novo (see also EPO 341,947) is a preferred lipase for use herein.

5 Peroxidase enzymes are used in combination with oxygen sources, e.g., percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching," i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-  
10 containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, published October 19, 1989, by O. Kirk, assigned to Novo Industries A/S.

A wide range of enzyme materials and means for their incorporation into synthetic detergent compositions are also disclosed in U.S. Patent 3,553,139, issued January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. Patent 4,101,457, Place et al, issued July 18,  
15 1978, and in U.S. Patent 4,507,219, Hughes, issued March 26, 1985, both. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. Patent 4,261,868, Hora et al, issued April 14, 1981. Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in  
20 U.S. Patent 3,600,319, issued August 17, 1971 to Gedge, et al, and European Patent Application Publication No. 0 199 405, Application No. 86200586.5, published October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. Patent 3,519,570.

Additionally, dye transfer inhibiting agents may also be included, for example, polyvinylpyrrolidone, polyamine N-oxide, copolymers of N-vinylpyrrolidone and N-vinylimidazole are a suitable dye transfer inhibiting polymers for use in the present detergent composition. The level of  
25 such additional dye transfer inhibiting agents may vary, but typically will be from about 0.01% to about 10% by weight of the detergent composition.

#### Agglomeration Process

The following describes and exemplifies the agglomeration process by which the detergent composition of the invention is produced. The parameters noted herein are exemplary only and  
30 should not be considered as limiting in any way.

Step A - Preparation of Surfactant Paste - The objective is to combine the surfactants and liquid in the compositions into a common mix in order to aid in surfactant solubilization and agglomeration. In this Step, the surfactants and other liquid components are mixed together in a Sigma Mixer at 140°F (60°C) at about 40 rpm to about 75 rpm for a period of from 15 minutes to  
35 about 30 minutes to provide a paste having the general consistency of 20,000-40,000 centipoise. Once thoroughly mixed, the paste is stored at 140°F (60°C) until agglomeration Step (B) is ready to be conducted.

Step B - Agglomeration of Powders with Surfactant Paste - The purpose of this Step is to transform the base formula ingredients including the water-soluble saccharides described herein into flowable detergent agglomerates having a mean particle size range of from about 800 microns to about 1600 microns. In this Step, the powders (including materials such as zeolite, citrate, citric acid builder, layered silicate builder (as SKS-6), sodium carbonate, ethylenediaminedisuccinate, magnesium sulfate and optical brightener) are charged into the Eirich Mixer (R-Series) and mixed briefly (ca. 5 seconds - 10 seconds) at about 1500 rpm to about 3000 rpm in order to mix the various dry powders fully. The surfactant paste from Step A is then charged into the mixer and the mixing is continued at about 1500 rpm to about 3000 rpm for a period from about 1 minute to about 10 minutes, preferably 1-3 minutes, at ambient temperature. The mixing is stopped when course agglomerates (average particle size 800-1600 microns) are formed.

Step C - The purpose of this Step is to reduce the agglomerates' stickiness by removing/drying moisture and to aid in particle size reduction to the target particle size (in the mean particle size range from about 800 to about 1600 microns, as measured by sieve analysis). In this Step, the wet agglomerates are charged into a fluidized bed at an air stream temperature of from about 41°C to about 60°C and dried to a final moisture content of the particles from about 4% to about 10%.

Step D - Coat Agglomerates and Add Free-Flow Aids - The objective in this Step is to achieve the final target agglomerate size range of from about 800 microns to about 1600 microns, and to admix materials which coat the agglomerates, reduce the caking/lumping tendency of the particles and help maintain acceptable flowability. In this Step, the dried agglomerates from Step C are charged into the Eirich Mixer (R-Series) and mixed at a rate of about 1500 rpm to about 3000 rpm while adding 2-6% Zeolite A (median particle size 2-5µm) during the mixing. The mixing is continued until the desired median particle size is achieved (typically from about 5 seconds to about 45 seconds). At this point, from about 0.1% to about 1.5% by weight of precipitated silica (average particle size 1-3 microns) is added as a flow aid and the mixing is stopped.

In order to make the present invention more readily understood, reference is made to the following examples, which are intended to be illustrative only and not intended to be limiting in scope.

#### EXAMPLE I

Several detergent compositions (A and B) are made in accordance with the agglomeration process described above. Composition B is within the scope of the invention and composition A is outside of the invention and is presented for purposes of comparison as described in Example II hereinafter. The relative proportions of compositions A and B, in agglomerate form, are listed in Table I below.



**TABLE I****(% weight)**

<u>Component</u>	<u>A</u>	<u>B</u>
C <sub>14-15</sub> alkyl sulfate	20.0	29.4
C <sub>16</sub> alkyl ethoxylate (EO = 0.6) sulfate	5.0	7.3
Aluminosilicate	44.9	47.2
C <sub>12-13</sub> linear alkylbenzene sulfonate	15.6	--
Sucrose	--	1.0
Sodium carbonate	14.1	15.0
Minors (water, perfume, etc.)	<u>0.4</u>	<u>0.1</u>
	<u>100.0</u>	<u>100.0</u>

**EXAMPLE II**

5           This Example illustrates the surprisingly improved solubility achieved by the detergent composition of the invention. Specifically, standard dosages of compositions A and B (1170 ppm) are dissolved in an aqueous laundering solution having a water temperature of 10°C and a water hardness of 7 grains/gallon (Ca:Mg ratio of 3:1). The laundering solution is continuously agitated at a rate of 75 rpm and samples of the wash solution were taken at various time intervals as shown

10 in Table I below. For purposes of illustrating the improved solubility of the detergent composition according to the invention, the amount of surfactant in the laundering solution is determined by conducting the well known "catSO<sub>3</sub>" titration technique on the samples taken from individual wash solutions containing one of the compositions A or B. In particular, the amount of anionic surfactant in the laundering solution is determined by filtering the samples through 0.45 nylon filter paper to

15 remove the insolubles and thereafter, titrating the filtered solution to which anionic dyes (dimidium bromide) have been added with a cationic titrant such as Hyamine™ commercially available from Sigma Chemical Company. Accordingly, the relative amount of anionic surfactant dissolved in the wash solution can be determined. This technique is well known and others may be used if desired. The results are shown in Table II below.

**TABLE II****(% total of anionic dissolved)**

<u>Time (Minutes)</u>	<u>A</u>	<u>B</u>
1	26%	16%
3	38%	34%
5	42%	57%
10	45%	71%

From the results in Table II, it is quite clear that composition B which is within the scope of the invention surprisingly has improved solubility over composition A which is outside the scope of the

25 invention.

**EXAMPLE III**

A laundry bar C suitable for hand-washing soiled fabrics is prepared by a standard extrusion process and comprises the following ingredients listed in Table III:

**TABLE III**

(% weight)

<u>Component</u>	<u>C</u>
C <sub>14-15</sub> alkyl sulfate	20.0
C <sub>16</sub> alkyl ethoxylate (EO = 0.6) sulfate	5.0
Aluminosilicate	44.9
C <sub>12-13</sub> linear alkylbenzene sulfonate	15.6
Sucrose	1.0
Sodium carbonate	14.1
Minors (water, perfume, etc.)	<u>0.4</u>
	<u>100.0</u>

Having thus described the invention in detail, it will be clear to those skilled in the art that various changes may be made without departing from the scope of the invention and the invention is not to be considered limited to what is described in the specification.

What is claimed is:

## Claims:

1. A detergent composition characterized by:
  - (a) from 1% to 50% by weight of a deterative surfactant system characterized by at least 30%, by weight of said surfactant system, of a sulfated surfactant selected from the group consisting of alkyl sulfates, alkyl ethoxy sulfates, secondary alkyl sulfates and mixtures thereof;
  - (b) from 0.1% to 5% by weight of a water-soluble saccharide selected from the group consisting of cellulbiose, glucose, maltose, lactose, ribose, and lactulose mixtures thereof; and
  - (c) at least 1% by weight of a detergency builder;wherein said surfactant system, said saccharide and said builder are agglomerated to form detergent agglomerates having a density of at least 650 g/l; wherein said sulfated surfactant of said surfactant system has improved solubility in an aqueous laundering solution.
2. A detergent composition according to claim 1 wherein said secondary alkyl sulfate surfactant is a secondary (2,3) alkyl sulfate.
3. A detergent composition according to claims 1-2 wherein said detergency builder is in an amount from 10% to 40% by weight.
4. A detergent composition according to claims 1-3 wherein said saccharide is sucrose.
5. A detergent composition according to claims 1-4 further characterized by adjunct ingredients selected from the group consisting of bleaches, bleach activators, suds suppressers and soil release agents.
6. A detergent composition according to claims 1-5 wherein said surfactant system is further characterized by weight of said surfactant system, from 1% to 50% of a C<sub>10</sub>-C<sub>18</sub> N-alkyl polyhydroxy fatty acid amide for use as an adjunct surfactant.
7. A detergent composition according to claims 1-6 wherein said sulfate surfactant is at least 5% more soluble in said detergent composition as compared to said sulfate surfactant dissolved alone in said aqueous laundering solution.

8. A detergent composition according to claims 1-7 wherein said saccharide is present in amount from 2% to 4%.
9. A detergent composition according to claims 1-8 wherein said detergent composition is in the form of a laundry bar.
10. A method for laundering soiled fabrics characterized by the step of contacting said soiled fabrics with an effective amount of a detergent composition according to claims 1-9 in an aqueous laundering solution.

## INTERNATIONAL SEARCH REPORT

Application No

PCT/US 95/06291

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D3/22 C11D17/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 215 637 (UNILEVER NV) 25 March 1987 see page 2, line 40 - page 3, line 9 ---	1,3-5,8
A	EP,A,0 245 551 (UNILEVER NV) 19 November 1987 see claims 1-9; examples ---	1,3-5,8
A	US,A,4 414 130 (CHENG BAO-DING) 8 November 1983 cited in the application see column 5, line 55 - column 6, line 16; claim 1 --- -/--	1,3,5

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

11 October 1995

Date of mailing of the international search report

18 -10- 1995

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+ 31-70) 340-3016

Authorized officer

Grittern, A

## INTERNATIONAL SEARCH REPORT

Int. Application No  
PCT/US 95/06291

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 8649 Derwent Publications Ltd., London, GB; Class D21, AN 86-322321 & JP,A,61 238 894 ( SUNSTAR KK) , 24 October 1986 see abstract ---	1
A	DATABASE WPI Section Ch, Week 8520 Derwent Publications Ltd., London, GB; Class A97, AN 85-119731 & JP,A,60 060 196 ( KANEBO KK) , 6 April 1985 cited in the application see abstract ---	1
A	DATABASE WPI Section Ch, Week 7738 Derwent Publications Ltd., London, GB; Class A97, AN 77-67455Y & JP,A,52 094 304 ( YUKEN KOGYO KK) , 8 August 1977 cited in the application see abstract ---	1
P,A	EP,A,0 622 454 (PROCTER & GAMBLE) 2 November 1994 see page 6, line 14 - page 7, line 10; claims 1,4,12; examples -----	1,3,5

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Application No  
PCT/US 95/06291

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0215637	25-03-87	AU-B- 591520	07-12-89
		AU-B- 6249486	12-03-87
		CA-A- 1275224	16-10-90
		DE-A- 3682246	05-12-91
		GB-A, B 2180254	25-03-87
		JP-B- 6037637	18-05-94
		JP-A- 62062900	19-03-87
		US-A- 4755318	05-07-88
-----			
EP-A-0245551	19-11-87	NONE	
-----			
US-A-4414130	08-11-83	AU-B- 519581	10-12-81
		AU-B- 2780277	15-02-79
		BE-A- 857881	16-12-77
		CA-A- 1105347	21-07-81
		CH-A- 636124	13-05-83
		DE-A- 2736903	23-02-78
		GB-A- 1568420	29-05-80
		NL-A- 7709091	21-02-78
		SE-A- 7709046	18-02-78
		SE-A- 8104374	15-07-81
-----			
EP-A-0622454	02-11-94	AU-B- 6780494	21-11-94
		WO-A- 9425553	10-11-94
-----			

**THIS PAGE BLANK (USPTO)**